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Experimental study of the effect of addition of nano-silica on the behaviour of cement mortars

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Abstract

The properties of cement mortars with nano-SiO_2 were experimentally studied. The amorphous or glassy silica, which is the major component of a pozzolan, reacts with calcium hydroxide formed from calcium silicate hydration. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Therefore, it is plausible to add nano-SiO_2 particles in order to make high-performance concrete. In the aim to study the effects of the addition of nanoparticles on the behavior of pastes and cement mortars, nano-particles of silica amorphous were incorporated at a rate of 3 and 10% by weight of cement. The compressive strengths of different mortars increase with the increasing of the amount of nano-SiO_2. The influence of nano-SiO_2 on consistency and setting time are different. Nano-SiO_2 makes cement paste thicker and accelerates the cement hydration process.

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Keywords: Nano-Silice; Compressive strength; Cement mortar; Setting time; Fresh properties

1. Introduction

Colloidal silica (CS) denotes small particles consisting of an amorphous SiO_2 core with a hydroxylated surface, which are insoluble in water. The size of the particles can be varied between 1 and 500 nm, hence they are small enough to remain suspended in a fluid medium without settling. Parameters such as specific surface area, size and size distribution can be controlled by the synthesis technique. Due

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to the high specific surface area for the nano-meter sized CS particles they constitute a highly reactive siliceous material. However, it has not yet been established whether the more rapid hydration of cement in the presence of nano-silica is due to its chemical reactivity upon dissolution (pozzolanic activity) or to a considerable surface activity. A recent contribution to the development of building materials comprises adding synthetic colloidal silica to concrete and cement mortars, whereby the resulting product displays improved aging properties with regard to strength gain, sulphate attack and alkali-silica reactions [1]. Recently, nano technology has attracted considerable scientific interest due to the new potential uses of particles in nanometer (10^{-9} m) scale. The nano scale-size of particles can result in dramatically improved properties from conventional grain-size materials of the same chemical composition. Thus, industries may be able to re-engineer many existing products and to design new and novel products that function at unprecedented levels. There are few reports on mixing nano-particles in cement-based building materials [2]. Thus, the use of nano-particles has received particular attention in many fields of applications to fabricate materials with new functionalities. When ultra-fine particles are incorporated into Portland-cement paste, mortar or concrete, materials with different characteristics from conventional materials were obtained [3]. The performance of these cementitious based materials is strongly dependent on nano-sized solid particles, such as particles of calcium–silicate–hydrates (C–S–H), or nano-sized porosity at the interfacial transition zone between cement and aggregate particles. Typical properties affected by nano-sized particles or voids are strength, durability, shrinkage and steel-bond. Nano-particles of SiO_2 can fill the spaces between particles of gel of C–S–H, acting as a nano-filler. Furthermore, by the pozzolanic reaction with calcium hydroxide, the amount of C–S–H increases, resulting a higher densification of the matrix, which improves the strength and durability of the material. Previous research indicates that the inclusion of nano-particles modifies fresh and hardened state properties, even when compared with conventional mineral additions. Colloidal particles of amorphous silica appear to considerably impact the process of C_3S hydration. Nano-silica decreased the setting time of mortar when compared with silica fume (SF) and reduced bleeding water and segregation, while improving the cohesiveness of the mixtures in the fresh state. When combined with ultra-fine fly ash it assures better performance than that achieved by the use of silica fume alone. Besides, the compressive strength of mortar or concrete with silica fume is improved when compared with formulations without addition. Some authors defend that the appropriate percentage of nano-SiO_2 has to be small (1–5 wt%) due to agglomeration caused by difficulties to disperse the particles during mix, while others indicate that the improvement of the properties can also be achieved with higher dosages, of about 10 wt%, if proper adjustments are made to the formulation in order to avoid excessive self-desiccation and micro-cracking that could hinder the strength [3].

In view of these advances, the aim of this study is to investigate the influences of nano-SiO2 in cement mortars. This paper reports the effects of nano-sized amorphous silica on the setting time and compressive and flexural strengths properties.

2. Materials and methods

2.1. Materials

The Portland cement used was CEM I 32.5 as classified by the Tunisian standard NT 47-01 and the European Standard EN 197-1. Its chemical composition and physical properties are shown in Table 1. Colloidal silica is suspension of fine amorphous, nonporous, and typically spherical silica particles in a liquid phase. It is defined as concentrated stable dispersion consisted of discrete and dense particles of amorphous silica SiO_2 of uniform particle sizes from 5 to 100 nm so with very high specific area. The solid concentration of these suspensions equals to 30%. The amorphous nano-scale silica, which is the major component of a pozzolan, reacts with calcium hydroxides formed from the hydration of calcium silicates. The rate of the pozzolanic reaction is proportional to the value of Blaine fineness. Therefore, the nano-SiO_2 used was of particle form with 99.9% SiO_2. Their pertinent properties, as provided by the manufacturer, are given in Table 2. Transmission electron micrograph (TEM) of nano-SiO_2 is shown in Fig.1.

Table 1. Chemical composition and physical properties of cementitious materials

Constituents	Content (%)
SiO2	16,51
Al2O3	3,59
Fe2O3	2,62
CaO	62,15
Mg O	1,05
K2O	0,50
SO3	3,53
Na2O	0,09
Cl-	0,03
Physical properties	
Specific gravity	3.02
Specific Surface Area (m2/g)	0.318

Table 2. The properties of nano-SiO_2

Avg. particle size (nm)	Specific surface Area (m2/g)	Density (g/cm3)	Content of SiO2 (%)
9	300	1,218	99,9

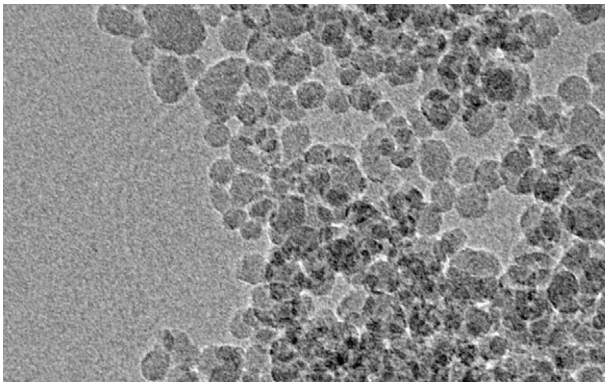

Fig. 1. TEM photographs of nano-SiO2.

A cement paste is composed of small grains of hydrated calcium silicate gels, nanosized individual pores, capillary pores (structural defects), and large crystals of hydrated products. There should be rooms for nanophase materials to improve the properties of pure cement paste [4]. However, as nano-particles are easy to aggregate due to their great surface energy, large quantity of these particles cannot be uniformly dispersed.

For mortar mixes, commercial and regular sand with a maximum size of 5 mm was used as aggregate in the mortar. The specific gravity of the regular sand was 2.6, the fineness modulus was 2.5, and the absorption capacity 0.2%.

2.2. Mortars formulations

The binder content was taken as the sum of cement and nanoparticles. Fresh mortars were prepared with binder/sand weight ratio (B/S) of 1:3 and water/binder (W/B) ratio of 0.5. All mortars were prepared with the same W/B ratio and produced with 0%, 3%, and 10% nano-SiO_2 in weight, replacing cement. The amount of water incorporated with nano-SiO_2 was taken into account by reducing the nominal content of water added to the preparation of the mortar. These compositions are shown in Table 3.

Table 3. Mortar formulations

Nano-SiO2 (wt%)	W/B	Mixture components			
		Water (ml)	Cement (g)	Sand (g)	Nano-SiO2 (g)
0	0,5	225	450,0	1350	0,00
3	0,5	225	436,5	1350	13,5
10	0,5	225	405,0	1350	45,0

2.3. Testing procedure

The cement mortars were mixed in a rotary mixer. Nano-particles are not easy to disperse uniformly due to their high surface energy. Accordingly, mixing was performed as follows:

- The nano-SiO2 particles were stirred with the mixing water at high speed for 1 min.
- The cement was added to the mixer and mixed at medium speed for another 30 s.
- Mixing at medium speed, the sand was added gradually.
- The mixture was allowed to rest for 90 s and then mixed for 1 min at high speed.

After the mixing stage, we seek to study the effect of percentage of nano-SiO2 on the workability and flow of various mortars. In order to characterize the workability of all studied mortars, we used the Maniabilimètre LCPC (French test). It is widely used to evaluate the workability of cement pastes, since it is easy to operate. This test consists of a rectangular mold with a movable wall and a vibrator. The test principle is, after removing the movable wall, to measure the time taken by the mortar under vibration to achieve a mark on the inner surface of the mold.

The wellmixed mortar was poured into molds to form the prisms of size 4 × 4 × 4 cm. For each mixture, twelve cubic specimens were made for compressive strength. An external vibrator was used to facilitate compaction and decrease the amount of air bubbles. After being demoulded at the age of one day, all specimens were cured in water at 20 ± 1 °C for 3, 7, 14 and 28 days.

In addition of the compressive strengths setting time tests were carried. Fresh pastes were prepared and produced with 0%, 3%, and 10% nano-Sio2 in weight, replacing cement with constant water/binder (W/B) ratio of 0.30. Setting time was determined by Vicat's needle, according to EN 196-3.

3. Results and discussion

Test results of flow (workability LCPC) are presented in table 4. They show that the flow time increases very rapidly with the increase in the percentage of nano-SiO_2.

Table 4. Flow time of mortars

Nano-SiO2 (wt%)	0 %	3 %	10 %
Flow time (s)	3	8	> 120

When nano-SiO_2 (wt%) is incorporated into the mortar in the fresh state it has a direct influence on the water amount required in the mixture. This behaviour confirms the fact that additions of high surface area mineral particles to cement mixtures cause the need for higher amounts of water or chemical admixtures in order to keep the workability of the mixture. If the water content is kept constant, as in the actual conditions, an increase of nano-SiO_2 content will promote the packing of particles, decreasing the volume between them and decreasing the free water. Therefore, there is a higher internal friction between solid particles.

3.1. Setting time

The influence of nano-SiO_2 addition on setting time of fresh pastes is presented in fig.2. With increasing the nano-SiO_2 content, the setting of fresh pastes was slightly accelerated but the difference between the initial and the final time decreased with increasing the NS content.

It appears that by adding nano-SiO_2, the beginning of setting is anticipated and the dormant period is reduced. So that it is possible to establish a relationship between initial setting time and the time for the beginning of the acceleration period during cement hydration.

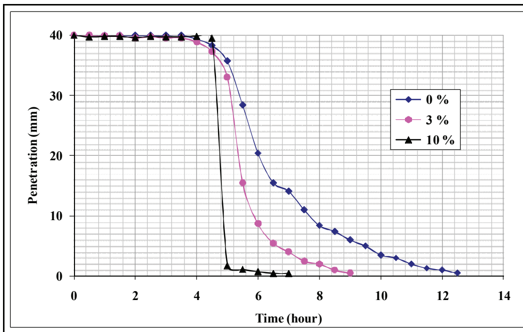

Fig. 2. Evolution of setting time

3.2. Compressive and flexural strengths

Figure 3 shows the relationships between compressive strengths and curing time for the three studied mortars. It can be seen that the compressive strength was developed in mortars containing nano-SiO2 particles in every case higher than that of control cement mortars. The difference in the strength development of the mortars can be attributed to pozzolanic reaction. Indeed, the nano-SiO_2 would fill pores to increase the mortar strength. Therefore, it is confirmed that the addition of nano-SiO2 to cement mortars improves their strength characteristics.

The strength of the mortars was found to increase as the nano-SiO2 content increased from 3% to 10%. However, it should be noted that using a higher content of nano-SiO2 must be accompanied by adjustments to the water dosage in the mix in order to ensure that specimens do not suffer excessive self desiccation and cracking. Otherwise, using this much quantity of nano-SiO2 could actually lower the strength of composites instead of improving it, although this finding was not observed in this study.

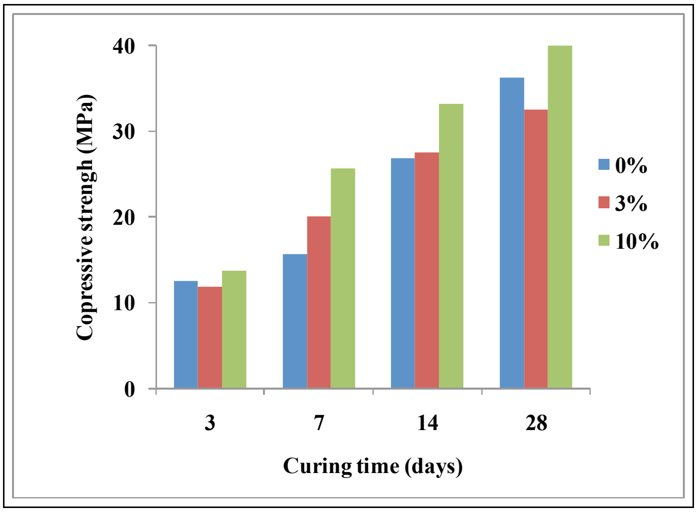

Fig. 3. Relationships between compressive strengths and curing time of mortars

4. Conclusions

The following conclusions may be drawn from the obtained experimental data:

- The influence of nano-SiO2 on consistency and setting time are different. Nano-SiO2 makes cement paste thicker and accelerates the cement hydration process. It can be explained by the fact that, in formulations having fixed values of W/B, the presence of nano-SiO2 decreases the amount of lubricating water available in the mixture.
- Compressive strengths increase with increasing the nano-SiO_2 content. It seems due to the action of nano-SiO_2 as an activator to promote hydration proves and to improve the microstructure of the cement paste if the nano-particles were uniformly dispersed.

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